EERO ASMALA

Transformation and removal of riverine dissolved organic matter in Baltic Sea estuaries

University of Helsinki,
Faculty of Biological and Environmental Sciences,
Department of Environmental Sciences

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Supervisor	Prof. David N. Thomas, Bangor University, U.K
Co-supervisor	Prof. Pekka Kauppi, University of Helsinki, Finland
Reviewers	Dr. Anne Ojala, University of Helsinki, Finland
	Dr. Martin Berggren, Lund University, Sweden
Opponent	Prof. Stiig Markager, Aarhus University, Denmark
Custos	Prof. Ilmo Massa, University of Helsinki, Finland

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Contents

List of original publications and author's contribution

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E.A. performed most of the field samplings and together with C.A.S. the data analyses, and was responsible for the manuscript preparation.

II **Asmala E.**, Autio R., Kaartokallio H., Pitkänen L., Stedmon C.A. & Thomas D.N. 2013. Bioavailability of riverine dissolved organic matter in three Baltic Sea estuaries and the effect of catchment land-use. Biogeosciences 10, 6969-6986.

E.A. participated in the experiment design, performed most of the field samplings, participated in laboratory analyses, performed the data analyses and was responsible for the manuscript preparation.

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E.A. designed the study, performed most of the field samplings, participated in laboratory analyses, performed the data analyses and was responsible for the manuscript preparation.

Symbols and abbreviations

%BDOC	Proportional bioavailable dissolved carbon
%BDON	Proportional bioavailable dissolved nitrogen
$a_{(CDOM254)}$	Absorption coefficient at 254 nm
$a_{(CDOM440)}$	Absorption coefficient at 440 nm
AMW_W	Weight-averaged apparent molecular weight
BDOC	Bioavailable dissolved carbon
BDON	Bioavailable dissolved nitrogen
BGE	Bacterial growth efficiency
CDOM	Colored dissolved organic matter
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
EEM	Excitation-emission matrix
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
Peak A	DOM fluorescence occurring at 380–460 nm from excitation at 260 nm
PO_4^{3-}	Phosphate
$S_{275-295}$	Absorption slope coefficient between 275–295 nm
$S_{300-650}$	Absorption slope coefficient between 300–650 nm
SD	Standard deviation
$SUVA_{254}$	DOC-specific absorbance at 254 nm
TDN	Total dissolved nitrogen
TN	Total nitrogen
TOC	Total organic carbon

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Abstract

The pool of riverine dissolved organic matter (DOM) results from integration of complex catchment processes, and links the terrestrial and coastal systems by transporting organic matter from watersheds to estuaries. In this thesis, field samplings and laboratory experiments were combined to assess the spatio-temporal variation in riverine DOM quantity and quality in three Finnish estuaries discharging to the Baltic Sea. Also, the biogeochemical transformation and removal processes influencing the composition of the DOM pool were studied. Large-scale catchment characteristics were linked to the properties of the riverine DOM. Throughout the work the DOM quality was assessed using multiple analytical approaches: C/N stoichiometry, colored DOM (CDOM) absorption, CDOM fluorescence, molecular weight and iron content. Estuarine DOM was subjected to heterotrophic degradation in factorial experiments to quantify the role of salinity, inorganic nutrients and predegradation to DOM bioavailability. Additionally salt-induced flocculation of DOM was studied by combining field samplings, laboratory experiments and modeling. The selected three study catchments differed markedly in their land-use, and these differences were reflected on the riverine DOM quantity and quality. The experiments provided evidence that increasing proportion of forests and peatlands were linked to the increase of carbon loading from the catchment, and to decreases in the subsequent quantities of bioavailable dissolved organic carbon (DOC) and bacterial growth efficiencies (BGE). A higher proportion of agricultural land in the catchment indicated an increase of the amount and bioavailability of dissolved organic nitrogen (DON) in the DOM pool. A larger proportion of lakes in the catchments were related to decreased bioavailable DON. Replete inorganic nutrients did not influence the DOM bioavailability, although did increase BGE on average from 11 to 40%. Increasing predegradation, i.e. DOM subjected to heterotrophic degradation for varying times before the actual bioassays, decreased BGE from 65 to 25% on average. Flocculation caused deviations from conservative mixing of DOM variables in the study estuaries, and the quantity and quality of flocculated DOM was studied in a laboratory experiment. The maximum deviation from conservative mixing of DOC in estuaries was -16% at salinities between 1 and 2, indicating significant flocculation within a relatively narrow salinity range. Both processes, biodegradation and flocculation, removed riverine DOM before reaching the open sea (so-called marginal filter), but also changed the properties of the remaining DOM pool. Also, both processes increased the humic-like fluorescence and DOC-specific absorbance of the DOM pool, which suggests that the refractory DOM pool reaching the sea is a result of multiple, interacting processes along the hydrological path. All in all, both biodegradation and flocculation remove riverine DOM in estuaries, and also transform the remaining DOM pool that ultimately reaches the open sea. Findings from this thesis show that DOM quality has a pivotal role in the functioning of both of these essential and ubiquitous mechanisms.

Keywords: aquatic systems, marginal filter, catchment, land-use, carbon, colored dissolved organic matter, bioavailability, flocculation

1 Introduction

Rivers and estuaries form the link between terrestrial and oceanic systems, transporting organic matter from the watersheds to marine environments. In Finland alone, rivers annually transport nearly one million tons of carbon in the form of organic matter to the Baltic Sea (Räike et al. 2012). Besides carbon, other major elements in organic matter are hydrogen and oxygen, and also nitrogen and phosphorus, resulting in a complex and variable mixture of different organic molecules (Hansell and Carlson 2002). Organic matter consists of particulate and dissolved phases (POM and DOM, respectively), which are traditionally separated on the operational criteria of filter pore sizes typically ranging between 0.2 to 0.7 µm. Riverine DOM entering estuaries is susceptible to different transformation and removal processes: adsorption to particulate matter (Krogh 1931; Gogou and Repeta 2010), photo-oxidative remineralization (Miller and Moran 1997), uptake by heterotrophs (Sepers 1977; Elifantz et al. 2007) and salt-induced flocculation (Sholkovitz et al. 1978; Abdulla et al. 2010). In this thesis, the latter two, transformation and removal of DOM by heterotrophic utilization and salt-induced flocculation will be discussed.

Aquatic organic matter in boreal catchments is primarily of terrestrial origin, which means that lakes, rivers and estuaries integrate the various physico-chemical and biological catchment-scale processes and shape the organic matter pool reaching the coastal sea (Kortelainen et al. 2013). Thus, catchment land-use has significant implications on estuarine water chemistry and organic matter fluxes (Johnes et al. 1996; Jickells 1998; Sachse et al. 2005). Differences in land-use have been shown to cause variation in dissolved organic carbon (DOC) export from boreal catchments, being on average 7.3 t km^{-2} and 3.8 t km^{-2} from peat-dominated and agricultural Finnish catchments, respectively (Räike et al. 2012). Also, catchment land-use partly influences the composition and complexity (i.e. quality) of riverine DOM (Graeber et al. 2012). In spite of the importance of catchment land-use in shaping the quantity and quality riverine DOM pool, the effects that catchments have on organic matter fluxes to estuarine and coastal environments are relatively poorly understood.

The physico-chemical properties of the highly heterogeneous DOM pool influence its reactivity in the environment, including its bioavailability (Tranvik 1990; Lønborg et al. 2009) and susceptibility to flocculation (Sholkovitz et al. 1978). For example, substrate quantity (i.e. concentration) affects bacterial utilization of DOM only if concentrations are very low, but on the other hand variation in DOM quality has been shown to explain the majority of the variability in bacterial growth dynamics (Hopkinson et al. 1998; Eiler et al. 2003). Also, humic-like and iron-containing DOM molecules are more prone to flocculation than bulk DOM (Forsgren et al. 1996). This quality-dependent selectivity of DOM removal processes implies that to accurately follow and predict the fate of DOM in estuarine environments its characteristics beyond the bulk properties must be resolved.

As the DOM pool consists of multitude of different types of molecules (Sleighter and Hatcher 2008), which vary from one environment to another, the exact determination of the constituents of the DOM pool is highly challenging. To tackle this problem, various methods are used that assess distinct DOM properties and are used as proxies for DOM characteristics (for a review, see Sulzberger and Durisch-Kaiser 2009). Absorption and fluorescence properties of DOM can be linked to its chemical characteristics, such as aromaticity (Weishaar et al. 2003) and molecular size (Helms et al. 2008), but can also be used to distinguish the origin of DOM (McKnight et al. 2001; Baker and Spencer 2004; Yamashita et al. 2013). The molecular size spectra of the DOM pool may also be analyzed directly with e.g. size-exclusion chromatography (Vartiainen et al. 1987). In this study, C/N stoichiometry (Sun et al. 1997), absorption and fluorescence spectroscopy (Green and Blough 1994) and molecular size distribution (Vartiainen et al. 1987) were used to link DOM characteristics to its bioavailability and susceptibility to flocculation.

The analysis of DOM quality proxies provides information on the bioavailability of DOM, as the underlying physico-chemical characteristics can in defined cases be coupled to e.g. available energy content of the individual DOM constituents. Bioavailability of DOM is a crucial factor shaping the coastal food web dynamics, as heterotrophic bacteria are typically limited by the availability of labile DOC (Lignell et al. 2008; Hoikkala et al. 2009). Simultaneously, phytoplankton is N/P limited, which leads to a situation where different groups in aquatic food webs are limited by different compounds. Ultimately, an increasing ratio between bioavailable DOC and inorganic nutrient could change the dynamic steady state of coastal food webs towards a microbially dominated food web (Elmgren 1989; Jonas 1997).

Heterotrophic utilization of DOM transforms carbon into bacterial biomass and CO_2, and the proportion of carbon directed to biomass can be measured with bacterial growth efficiency, BGE (del Giorgio and Cole 1998). This transformation of DOM to bacterial biomass supports heterotrophic food webs, which are essential to the productivity of aquatic ecosystems (Mann 1988). Bulk properties of the DOM pool have been shown to influence BGE (Kroer 1993), but also a range of environmental variables affect BGE, including temperature, inorganic nutrient availability, salinity and the DOM source (del Giorgio and Cole 1998; Wikner et al 1999). Thus, the DOM quality is essential to carbon cycling in the aquatic environment and the functioning of heterotrophic food webs, as it may affect both the bioavailability of DOC and the performance of the heterotrophic community (with BGE being used as a proxy, Moran and Hodson 1990; Tranvik 1990; Søndergaard et al. 2000).

In general, large, aromatic allochthonous DOM compounds are considered less bioavailable than small, aliphatic autochthonous DOM compounds (Amon and Benner 1996; Ortega-Retuerta et al. 2009; Guillemette and del Giorgio 2012). Also, the diagenetic state, i.e. the extent to which the DOM pool has been degraded is of importance since DOM subjected to biodegradation is generally less bioavailable than fresh DOM (Amon et al. 2001; Berggren et al. 2009). Even though autochthonous, algal-derived DOM can be more bioavailable than allochthonous DOM, labile terrestrial DOM is typically much more abundant than algal DOM in the estuarine environments dominated by the terrestrial influx of organic matter (Guillemette et al. 2013). This underlines the significance of riverine DOM flux providing a replete and steadier source of carbon for coastal food webs, which potentially has a larger impact on long-term carbon cycling in estuaries.

Besides bioavailability, DOM quality also affects the salt-induced flocculation of riverine organic matter in estuarine environments (Gregory 1989). Flocculation is one of the processes that form the so-called “marginal filter” in estuaries, where significant proportions of riverine inorganic (e.g. iron, phosphorus) and organic constituents are removed before entering the coastal waters (Lisitsyn, 1995). Flocculation and the subsequent sedimentation of organic matter in estuaries can have implications for the benthic food webs, and riverine organic matter load may locally be the dominant source of carbon in coastal sediments (Schreiner et al. 2013). Further, the increased heterotrophic activity in the benthic zone due to flocculation and sedimentation of organic matter can locally contribute to coastal hypoxia (Tranvik and Sieburth 1989; Jonas 1997). Considering the vast amounts of terrestrial carbon transported via rivers to coastal seas, even the conservative estimates of proportional flocculation of riverine carbon (3 to 6 % by Sholkovitz et al. 1978) transfers substantial amounts of terrestrial carbon from dissolved phase into coastal sediments. Also, as the most active salinity range for flocculation is around 5 (Lisitsyn 1995), the carbon burial to the sediment may occur in a relatively narrow geographical range close to the river mouths.

The qualitative aspects of DOM that have an effect on flocculation are linked with the surface charge properties of individual DOM molecules. As the negative surface charge of DOM molecules are neutralized by salt ions in the estuarine water, aggregation and subsequent flocculation becomes more probable (Gregory 1989). Large, humic-like DOM molecules are relatively more susceptible to flocculation than smaller, non-humic DOM (Sholkovitz et al. 1978). DOM molecules containing iron are also flocculated rapidly in the estuarine salinity gradient (Forsgren et al. 1996). These qualitative properties of DOM contributing to flocculation can be studied utilizing CDOM spectroscopy, as both humic-like properties and presence of iron increase the UV absorption of DOM (Weishaar et al. 2003; Xiao et al. 2013). Analyzing these changes in DOM quality during estuarine transport, a detailed view of the selectivity of the flocculation process can be formed.

The time-scales of biodegradation and flocculation are different to some extent; flocculation is assumed to reach a dynamic steady state in a time-scale of hours in constant salinity (Gregory 1989), whereas biological degradation continues to shape the DOM pool for significantly longer periods. Traditionally, DOM has been classified to labile, semi-labile and refractory pools, depending on the processing time needed prior bacterial utilization (Søndergaard and Middelboe 1995; Vähätalo et al. 2010; Hansell 2013). Similar, operational classifications of DOM flocculation kinetics have not been established. After being exposed to different degradation processes, the most refractory components of DOM pool remain, and can resist degradation for extensive periods, even for millennia (Jiao et al. 2010; Hansell 2013). As these both processes are occurring simultaneously in estuarine environments, it is important to acknowledge the fundamental difference of threshold-dependent flocculation process and biological degradation continuum of DOM.

Continuous loading of riverine DOM to estuaries provides a replete source of substrates for heterotrophic bacteria and a flux of organic matter via flocculation to coastal sediments. Also, the transport along the estuarine gradient transforms the DOM that resists the removal processes, thus shaping the remaining DOM pool reaching the open sea. The work reported in this thesis was designed to improve the insight on the effect of DOM quality to the removal processes, but also to evaluate the DOM transformation by studying the changes in DOM quality along the estuarine gradient.

More specifically, the objectives of the study were:

- To measure the variability in quantity and quality of riverine DOM entering the Baltic Sea (papers I, III)
- To clarify the link between DOM quality and its heterotrophic utilization in estuaries (papers II, IV)
- To quantify the DOM flocculation in low salinities of the Baltic Sea estuaries (papers III)

2 Material and methods

2.1 Study area (papers I-IV)

Three estuaries draining to the Baltic Sea were studied: Karjaanjoki, Kyrönjoki and Kiiminkijoki. The selected three catchments have differing land-use which result in different water properties in estuaries (HERTTA 2013). The Karjaanjoki catchment area is the most urbanized of the three and has most lakes in its catchment area. Karjaanjoki has the lowest TOC and TN loadings of the rivers studied for the study period (2.0 and 0.18 t y^{-1} km^{-2}, respectively). The Kyrönjoki catchment is dominated by agriculture, with both fertilized pastures and crops, resulting in high TOC and TN loadings (5.2 and 0.60 t y^{-1} km^{-2}, respectively). In contrast the Kiiminkijoki catchment consists mostly of peatlands and forests, which results in high TOC and low TN loadings (6.2 and 0.21 t y^{-1} km^{-2}, respectively).

2.2 Field sampling (papers I-IV)

The estuaries were sampled along a salinity gradient from the river mouth to sea end-member in the coastal Baltic Sea, as described in I-IV. The longest sampled gradient was the Karjaanjoki estuary, the distance between river and sea end-member being 38 km, and the salinity of the coastal waters being on average 6.3 ±0.5. In the Kyrönjoki and Kiiminkijoki estuaries the end-members were 36 and 21 km apart and salinity of the sea samples were 2.7 ±1.1 and 2.3 ±0.1 respectively. In all cases the river waters were sampled from the main channels, close to the river mouths. The estuaries were sampled on six occasions: in April/May 2010, August 2010, October 2010, April/May 2011, August 2011 and October 2011. Spring samplings occurred on, or very close to, spring freshet, summer samplings during annual minimum flow and autumn samplings before the catchments froze. A total of 178 samples were collected on the six transect sampling trips.

2.3 Experimental studies (papers II-IV)

For the main biodegradation experiment (II), we used a factorial design of water types (sea end-member, river end-member and their 1:1 mix), salt additions and nutrient (NO_3^- and PO_4^{3-}) additions. This set-up allowed us to study the individual and combined effects of changes in salinity and inorganic nutrient availability along the artificial three-point estuarine gradient. DOM flocculation experiment (III) was conducted on water from Kiiminkijoki river end-member. Filtered river water was spiked with strong salt solution (salinity 105) to create an artificial salinity gradient from 0 to 6. The effects of bacterial predegradation to DOM bioavailability was studied in an experiment where water from Kiiminkijoki river was subjected to bacterial predegradation for varying times between 3 and 15 months (IV).

River discharges typically display significant intra-annual variability, and sporadic, extreme events such as heavy rainfall can cause additional major fluctuations in DOM quantity and quality entering aquatic systems (Conmy et al. 2009; Jennings et al. 2012). Our study design allowed the inter-comparison of contrasting seasons: The spring season after ice-melt is characterized by relatively high discharge and labile DOM. During the summer the discharge is low and photolysis and autotrophic activity are the main processes changing DOM characteristics. In autumn discharge increases and the seasonal decrease in estuarine autotrophic and photolytic activity shifts the DOM characteristics closer to terrestrially-derived organic matter (Wikner et al. 1999; Sachse et al. 2005). Also, catchment-scale processes in general outweigh the episodic, small-scale processes in shaping the riverine DOM pool (Burrows et al. 2013; Kortelainen et al. 2013).

2.4 Laboratory measurements (papers I-IV)

To determine the quantitative and qualitative values of the DOM pool in study estuaries, an array of analytical methods was used, as described in papers I-IV (Table 1). In addition, the abundance and performance of the bacterial community (leucine and thymidine incorporation, community respiration and cell enumeration) was studied in II and IV.

2.5 Statistical analyses (papers I-IV)

To predict DOC concentration from CDOM parameters (I), we used single and multiple linear regression models (SLR and MLR, respectively). The performance of both SLR and MLR models were analyzed with standard error of the estimate, and we tested the predictor variables for inter-correlation using variance inflation factors for MLR models. To quantify the statistical significance of the differences between observed and predicted values of DOM variables in estuarine transects in order to assess the deviations from conservative mixing (III), we used one sample Wilcoxon signed-rank test. For studying the statistically significant differences between groups, we performed analyses of variance (single factor ANOVA and one-way Kruskal-Wallis; I, II and IV), analysis of covariance (II), Welch's *t* test (II) and for post-hoc analysis we used Tukey's HSD (II). Statistical analyses were done using the PASW18 software and the basic functions of R software (R Core Team 2012).

Table 1. Summary of the methods used in papers I-IV.

Parameter	Method	**References**
Bacterial abundance	Flow cytometry	Gasol et al. (1999), Gasol and del Giorgio (2000)
Bacterial production	Leu+TdR incorporation	Fuhrman and Azam (1980), Kirchman et al. (1989)
CDOM absorption	Spectrophotometric detection	Stedmon et al. (2000)
CDOM fluorescence	Spectrofluorometric detection	Murphy et al. (2010)
Dissolved organic carbon	High temperature combustion	Qian and Mopper (1996)
Dissolved oxygen	Winkler titration with a potentiometric titrator	Graneli and Graneli (1991)
DOM molecular weight	Size-exclusion chromatography	Vartiainen et al. (1987)
Total dissolved iron	Inductively coupled plasma atomic emission spectroscopy	US EPA (2003)
NH_4^+	Colorimetric determination	Grasshoff et al. (1983)
NO_2^- + NO_3^-	Colorimetric determination	Grasshoff et al. (1983)
PO_4^{3-}	Colorimetric determination	Grasshoff et al. (1983)
Total dissolved nitrogen	Colorimetric determination after persulphate oxidation	Koroleff (1979)

3 Results

3.1 Spatial variability of DOM quantity and quality (I-III)

There were significant differences in DOM quantity and quality between estuaries, as described in papers I-III. The differences in selected DOM variables in river and sea end-members are presented in Table 2. Differences of selected DOM variables between seasons were not statistically significant, and therefore not detailed here.

3.2 Biodegradation of DOM (papers II, IV)

We found no evidence of the bulk concentration (with DOC concentration as a proxy) affecting DOM degradation, whereas DOM quality had significant impact on the DOM bioavailability (Table 3). In general, when the DOM pool consisted on average of large, humic-like molecules with high C:N ratio, the BGE was low. Pre-degradation (degradation of labile DOM compounds prior to actual degradation study; Figure 7 in IV) and inorganic nutrient availability did not significantly effect %BDOC, but did influence BGE (inverse and direct, respectively). On average, 9.1 ±5.0 % of DOC was degraded during the 12 to 39 day bioassays. During the heterotrophic DOM degradation, also the qualitative parameters of DOM changed; molecular size and UV slope decreased, and humic-like fluorescence and $SUVA_{254}$ increased on average.

3.3 Flocculation of DOM (papers I, III)

Non-conservative behavior of riverine DOM was observed in study estuaries (I, III), and following this, the salt-induced flocculation of riverine DOM was studied in a laboratory experiment (III). A maximum deviation of -16% was observed in DOC concentrations in study estuaries between salinities 1 and 2 (Figure 4 in III), indicating that there was a removal of DOC at low salinities. This finding was confirmed in

Table 2. Mean values of selected DOM variables in study estuaries' end-members (*n* = 6 for each value). ± indicates 1 standard deviation. Sig. = significance of differences between estuaries determined with Kruskal-Wallis analysis of variance: *** = p < 0.001, * = p < 0.05 and n.s. = non-significant (p > 0.05).

River end-member				
	Estuary			
DOM variable	**Karjaanjoki**	**Kiiminkijoki**	**Kyrönjoki**	**Sig.**
DOC (µmol l^{-1})	654 ±111	1368 ±331	1575 ±512	***
DON (µmol l^{-1})	28.6 ±4.8	30.7 ±3.2	50.5 ±11.1	***
$a_{(CDOM254)}$ (m^{-1})	64.1 ±16.8	183.8 ±33.6	199.4 ±82.1	*
$a_{(CDOM440)}$ (m^{-1})	3.7 ±2.3	13.5 ±2.1	12.5 ±6.2	*
$SUVA_{254}$ (mg l^{-1} m^{-1})	3.54 ±0.48	5.03 ±1.16	4.42 ±0.54	*
$S_{275-295}$ (μm^{-1})	17.3 ±1.7	12.0 ±0.3	13.5 ±0.9	***
$S_{300-650}$ (μm^{-1})	16.0 ±1.7	14.7 ±0.3	15.8 ±0.6	*
Peak A (R.U.)	1.37 ±0.85	1.94 ±0.28	2.84 ±0.74	*
AMW_W (Da)	2335 ±156	2860 ±213	2686 ±328	*
Fe (µg l^{-1})	204 ±245	1188 ±369	820 ±431	*
Sea end-member				
	Estuary			
DOM variable	**Karjaanjoki**	**Kiiminkijoki**	**Kyrönjoki**	**Sig.**
DOC (µmol l^{-1})	340 ±20	407 ±101	489 ±221	n.s.
DON (µmol l^{-1})	21.4 ±3.2	14.9 ±1.2	15.8 ±1.4	*
$a_{(CDOM254)}$ (m^{-1})	21.8 ±2.8	38.0 ±3.8	44.0 ±29.2	*
$a_{(CDOM440)}$ (m^{-1})	0.8 ±0.3	2.0 ±0.6	2.3 ±0.3	*
$SUVA_{254}$ (mg l^{-1} m^{-1})	2.31 ±0.18	3.66 ±1.06	2.99 ±0.82	*
$S_{275-295}$ (μm^{-1})	24.4 ±1.1	17.8 ±1.2	18.5 ±3.6	***
$S_{300-650}$ (μm^{-1})	18.0 ±2.5	16.3 ±1.5	17.5 ±2.7	n.s.
Peak A (R.U.)	0.33 ±0.03	0.57 ±0.05	0.68 ±0.46	*
AMW_W (Da)	1740 ±51	2116 ±53	2059 ±152	*
Fe (µg l^{-1})	2.0 ±2	37 ±40	99 ±98	*

Table 3. Linear effects of DOM quality parameters on proportion of bioavailable DOC (%BDOC) and bacterial growth efficiency (BGE). Molecular size is measured by size-exclusion chromatography, fluorescence peak A (Coble 1996) is used as a proxy for humic-like fluorescence, UV slope $S_{275–295}$ is the CDOM absorption slope coefficient between 275 and 295 nm, $SUVA_{254}$ is the DOC-specific UV absorbance at 254 nm, predegradation is the degradation of labile DOM compounds prior to actual degradation study and inorganic nutrient availability means replete inorganic nitrogen and phosphorus conditions during incubations. Inverse = inverse relationship, i.e. high quality value results as low response value. Direct = direct relationship, i.e. high quality value results as high response value. N/A = no effect. Change (%) indicates the average proportional change in respective DOM quality parameter during incubations.

DOM quality parameter	**Effect on %BDOC**	**Effect on BGE**	**Change (%)**	**Study**
DOC:DON ratio	N/A	Inverse	-0.7 ±0.8	II
Molecular size	N/A	Inverse	-0.9 ±0.5	II
Humic-like fluorescence	N/A	Inverse	2.8 ±0.9	II, IV
UV slope $S_{275–295}$	Direct	Direct	-0.4 ±0.2	II, IV
$SUVA_{254}$	Inverse	Inverse	7.9 ±0.9	II, IV
Predegradation	N/A	Inverse	N/A	IV
Inorganic nutrient availability	Direct	Direct	N/A	II, IV

the laboratory experiment, where riverine dissolved organic matter was flocculated from the dissolved fraction by the addition of salt water. In the experiment also qualitative changes in the DOM pool was measured, indicating preferential flocculation of iron-containing organic colloidal material. Proxy for DOM aromaticity ($SUVA_{254}$) increased due to flocculation, as UV-absorbing DOM was flocculated less than non-UV-absorbing DOM (Table 4). Using the measurements from the experiment, a mechanistic model was built which explains the flocculation of DOM in low salinities by linking the collision dynamics of DOM molecules with changing surface charge conditions along the salinity gradient.

Table 4. Initial values at salinity 0 (before salt addition) and cumulative, relative net changes (in %) of selected DOM variables in salinities 2 and 6 due to flocculation in an experimental set-up.

DOM variable	**Initial = salinity 0**	**Change at salinity 2**	**Change at salinity 6**
DOC	15.0 ±0.1 (mg l^{-1})	-6.3 %	-13.8 %
AMW_w	2978 ±16 (Da)	-9.7 %	-17.3 %
$a_{(CDOM254)}$	179.1 ±0.2 (m^{-1})	-3.2 %	-7.0 %
$SUVA_{254}$	5.20 ±0.01 (l mg^{-1} m^{-1})	3.2 %	7.9 %
Fe	1.33 ± 0.00 (mg l^{-1})	-13.8 %	-36.8 %

4 Discussion

4.1 Linking catchment land use and estuarine DOM (I-III)

Riverine DOM entering the Baltic Sea through the study estuaries was shown to vary in quantity and quality (I-III). The high DOC loadings of Kyrönjoki and Kiiminkijoki estuaries were linked to the relatively high proportions of cropland and pastures (Kyrönjoki), forests and peatlands (Kiiminkijoki), and low proportion of lakes in the catchment (Mattsson et al. 2005). On the other hand, a low percentage of wetlands and high percentage of lakes (3 and 11 %, respectively) in the Karjaanjoki catchment were associated with lower DOC loadings. The differences in DOM quantity (DOC concentration as a proxy) were also linked to differences in DOM quality: Rivers with high DOM quantities also had high humic-like properties in the bulk DOM pool. This coupling implies a ubiquitous terrestrial source of DOM (Graeber et al. 2012), and the concentration and humic-like properties of DOM both being proxies of the extent of its degradation, i.e. the spatial and temporal distance from the source.

Catchment land-use affects also the nutrient status of the receiving rivers and estuaries, and this in turn affects the carbon cycling at the landscape level (Kortelainen et al. 2013). In our studies, the agricultural Kyrönjoki had the lowest C:N ratio of the study catchments (I, II), indicating an increasing effect of agriculture to the nutrient status of the receiving water system. Agriculture typically increases DON leaching from the soils, but has no similar effect on DOC leaching (McDowell et al. 2004), which was also evident in our study (II). The importance of land-use in shaping the DOM pool in rivers and estuaries can be conceptualized with the so-called *reactive transport* where DOM is constantly decomposed, altered or produced before entering the aquatic system (Malik and Gleixner 2013). In addition to the actual land-use patterns, the length of the hydrological path within the soil is also a key factor, since the longer the residence time in soil the further the DOM is processed before entering the fluvial system. In our study catchments, the hydrological path can be expected to be relatively short in Kyrönjoki and Kiiminkijoki, due to high proportion of wetlands (19 and 40 %, respectively, Laudon et al. 2007). Besides the catchment-scale processes, the reactive transport is also dependent on the small-scale properties of the riparian flow path (e.g. vegetation, steepness) that shape the DOM pool before reaching the rivers and estuaries (Findlay et al. 2001). However, catchment-scale processes are more important in shaping the inflowing DOM pool than episodic, small-scale processes (Burrows et al. 2013; Kortelainen et al. 2013), which justifies the use of the wider scope in this study to link the catchment characteristics to properties of the riverine DOM pool.

Besides quantity, the quality of DOM entering the estuaries also varied between the study catchments (I-III). For instance, the humic-like properties of DOM were the weakest in Karjaanjoki estuary, where the high lake percentage allows increased processing of DOM decreasing its terrestrial, humic-like signal (Köhler et al. 2002; Mattsson et al. 2005). On the other hand, the combined effect of low proportion of lakes and high proportion of agriculture or peatlands in the Kyrönjoki and Kiiminkijoki catchments led to high humic-like signals in the riverine DOM (Kalbitz et al. 1999; Wilson and Xenopoulos 2008; Hanley et al. 2013). Humic-like properties are also strongly linked with the dynamics of iron in the dissolved fraction (Heikkinen 1994; Laglera et al. 2009), which was evident in the high correlation between optical properties and iron concentrations in studies I and III.

In paper I, we confirmed the strong, catchment-scale link between DOC and CDOM yields (Stedmon et al. 2011). Following this, the CDOM yield could be more easily used to monitor DOC loadings from catchments than the direct measurements of DOC, which would answer the growing need for knowledge of the catchment impacts on the coastal systems (Harris and Heathwaite 2012; Gibbs 2013). Furthermore, CDOM characteristics can also be linked to lignin content of the DOM pool, which is a direct proxy of vascular plant origin (Fichot and Benner 2012; Hernes et al. 2013) and hence provides a proxy for the terrestrial signal of DOM in the coastal waters. In our study, bulk properties of the DOM pool were dominated by catchment-derived riverine signal in upper estuaries, but the transect end-members already expressed the characteristics of the respective Baltic Sea basin (I, III). These properties include DOC concentration, humic-like fluorescence and molecular size. Thus, the properties of the DOM pool in estuaries are a result from different processes, including mixing of the two end-members, riverine and marine.

4.2 Effects of DOM quality to bioavailability (papers II, IV)

Bioavailability of riverine DOM was studied in two experimental set-ups (II, IV), in which the effect of season, salinity, inorganic nutrient availability, catchment land use and pre-degradation were assessed. The focus of the studies was to link DOM qualitative properties to bioavailability, indicated by proportional DOC degradation (%BDOC). Furthermore, the role of DOM quality on the performance of bacterial community with bacterial growth efficiency (BGE) was investigated, BGE being a metric for the efficiency of carbon transferred from substrate (DOM) to bacterial biomass. The bacterial community composition in the Baltic Sea is only weakly linked to the processing of the bulk DOM pool (Dinasquet et al. 2013), which suggests that there are general patterns of DOM utilization throughout different bacterial taxa. Surprisingly, we did not find that season (including the varying temperature) to have an effect either on %BDOC or BGE. This is contrary to commonly observed temperature dependences found by others (e.g. Raymond and Bauer 2000; Apple et al. 2006; Berggren et al. 2010a). Also the relatively minor changes in salinity introduced in the experimental set-up did not affect DOM degradation.

Inorganic nutrient additions (NO_3^- and PO_4^{3-}) increased both %BDOC (IV) and BGE (II, IV), which concurs with the general view of nutrients enhancing the DOM cycling (e.g. Kuparinen and Heinänen 1993; Zweifel et al. 1993, 1995). Availability of inorganic nutrients increased the degradation of both fresh and pre-degraded ("old") DOM (IV), which suggests that the scarcity of available nitrogen and phosphorus constrains DOM cycling throughout the diagenetic spectrum (Amon et al. 2001). Availability of nitrogen and phosphorus was linked to land-use via agriculture and lakes, as proportion of agricultural land had direct effect on DON bioavailability and proportion of lakes an inverse effect (II). Also, it can be speculated that the high inorganic loading from agricultural land enhances the DOM cycling in the receiving estuary. An increasing proportion of forests and peatlands in the catchments resulted in a decreasing DOC and DON bioavailability, indicative of a relatively refractory DOM pool originating from these land-use types. The high DOC:DON ratio of DOM in the Kiiminkijoki estuary – which is dominated by forests and peatlands – implies that heterotrophic activity relies on DOM of relatively poor quality for sufficient energy demand (c.f. Hopkinson et al. 1997).

The effect of pre-degradation (i.e. the diagenetic status) did not affect %BDOC, but had an influence on BGE. Increasing pre-degradation, i.e. increasing diagenetic status decreased BGE (IV), indicating a change towards inferior DOM quality (Cowie and Hedges 1994; Amon et al. 2001; Köhler et al. 2013). Based on these results, the DOM pool can be viewed as a "buffet table", where the compounds with the better energetic value and/or elemental composition are consumed first. Replete inorganic nutrients partially compensated the effect of predegradation, which indicates that the predegradation decreases the availability of N and P from the DOM pool (Thingstad and Lignell 1997; Jansson et al. 2006). The effect of predegradation can be linked to climate change and land use, as both potentially have implications for DOM residence time in catchments, which in turn has consequences for the extent of predegradation (Tranvik and Jansson 2002; Algesten et al. 2003; Tranvik et al. 2009).

As DOC concentration alone did not affect or constrain DOM degradation (II, IV), it can be argued that bacteria were not C-limited in estuaries. However, bacterial growth may have been limited by labile carbon, which is not necessarily reflected in the bulk DOC concentration (Lignell et al. 2008). This qualitative difference in DOM pool that leads to its classification to labile, semi-labile or refractory is based on operative definitions based on the turnover times of different DOM compound groups in defined environments (Søndergaard and Middelboe 1995; Hansell 2013). However, the inherent properties of DOM do not exclusively determine its bioavailability (i.e. lability). For instance, when ancient DOM is released by an episodic event from peat mire to the lotic system, it is biodegraded at the same rate or even more rapidly as more modern DOM (Hulatt et al. 2014; Vonk et al. 2013). From this follows, that such classifications to labile or refractory may only be valid in the context of the ambient environment (Bianchi 2011). In the framework of this study, the changing inorganic nutrient status is an example of a critical change in the environmental conditions enabling the degradation of previously non-degradable DOM (II, IV). This so-called priming effect changes the reactive status of DOM (Bianchi 2011), i.e. strong short-term changes are achieved with comparatively moderate treatments (Kuzyakov et al. 2000).

Optical properties of DOM, such as humic-like fluorescence, DOC-specific UV absorbance and UV-slope, were to an extent linked to its bioavailability (Table 2, II, IV). In general, there was a common trend for the larger, more aromatic and humic-like bulk DOM resulting in lower %BDOC and BGE. This also is true of the molecular weight of DOM, as larger molecules resulted in lower BGE estimates (Table 2). This indicates that when DOM pool consists of relatively large and humic-like molecules the quality is less optimal for heterotrophic utilization than a pool with smaller, non-aromatic DOM molecules (Berggren et al. 2010b; Fellman et al. 2010). Optical properties of DOM have previously been linked to e.g. DOC concentration (Banoub 1973; I) and other physico-chemical characteristics (Carder et al. 1989; Weishaar et al. 2003; Helms et al. 2008) of the DOM pool. Understanding the coupling between DOM characteristics and its optical properties are crucial when using remote sensing to assess e.g. phytoplankton production in optically complex waters heavily influenced by CDOM-rich riverine fluxes (Cannizzaro et al. 2013). However, remote sensing is currently not likely to provide as detailed information about DOM optical properties as direct measurements, since satellite information does not cover the UV area of the spectrum (e.g. Johannessen et al. 2003; Kutser et al. 2005), where signal-to-noise ratio is the highest and also the more detailed spectral characteristics occur. Linking the bulk properties of the DOM pool to its ecological significance – in terms of bioavailability as proposed in this study – via cost-effective optical measurements would provide a powerful tool to monitor organic matter dynamics in the highly heterogeneous land-sea continuum with unprecedented resolution.

4.3 Role of flocculation in DOM transport through estuaries (papers I, III)

The behavior of riverine DOM deviated from conservative mixing in study estuaries (I, III), and the deviations observed in the field data were confirmed in a laboratory experiment (III). Our data supports the concept of the "marginal filter" (Lisitsyn 1995), which determines upper estuaries (salinities from 0 to 5) as sites of highly active flocculation of organic and inorganic constituents of the riverine load. Up to 16 % loss of DOC from expected values was observed in the field data, which concurs with earlier findings (e.g. Sholkovitz 1976; Forsgren et al. 1996). From Finnish rivers only, nearly 1 million tons of riverine DOC flows to the Baltic Sea annually (Räike et al. 2010), and even the most conservative estimates of flocculation rate of organic carbon results as a net C deposition in order of 10^5 tons to the coastal areas each year. For comparison, gross primary production of the Gulf of Finland and Gulf of Bothnia (Baltic Sea basins that Finnish rivers drain to) is estimated to be in order of 10^7 tons of C annually (Savchuk et al. 2012). These results show that the sedimentation of flocculating riverine organic carbon can, by quantity, be of high importance in supplying the benthic food web with continuous flux of organic matter (Bartels et al. 2012).

As riverine DOM load differs not only in quantity, but also in quality between catchments and this variation can be linked to differences in land use (I-III), we suggest that catchment land use has implications also to the estuarine flocculation process. The humic-like, iron-containing DOM is most easily flocculated (Sholkovitz et al. 1978), and these properties are characteristic to DOM flux from boreal catchments with organic soils (Heikkinen 1994; Kortelainen et al. 2006). Surprisingly, evidence for preferential flocculation of humic-like DOM was not found in our experimental study, but was observed in field samples. This might be due to particle interactions in the estuarine environment (Lisitsyn 1995). In our study, we found the flocculation maximum at the salinity range 1–2, which is the range which Lisitsyn (1995) describes as the "silt plug" where flocculation of e.g. organic acids and iron coincide in space. This co-precipitation and chelation of iron and dissolved organic carbon promote the preservation of these formed carbon-iron associations in sediments, effectively creating a "rusty sink" lasting for geological timescales (Lalonde et al. 2012). However, iron dynamics in the sediment are highly dependent on the oxic conditions, and in the Baltic Sea this can cause fluctuations in the iron transport between water and sediment (Lehtoranta and Pitkänen 2003; Fehr et al. 2008). Despite the strong affinity to flocculation, terrigenous (riverine) Fe is suggested to be the main source for Fe in the ocean (De Baar and De Jong, 2001).

Besides reducing the concentration of riverine DOM in estuaries, flocculation also changes the composition of the remaining DOM pool. We could identify two processes contributing to this qualitative change: 1) selective removal of DOM constituents, and 2) altering the properties of some of the remaining DOM constituents. Selective removal during flocculation is observed to pick out especially humic and/or iron-containing organic molecules from the DOM pool (Sholkovitz et al. 1978; Forsggren et al, 1996; Uher et al., 2001). However, our study suggests that increasing salinity does not just remove DOM, but also changes the properties of the remaining DOM pool (Figure

1). Humic-like fluorescence of the remaining DOM pool increased compared to the situation prior to salt addition. From this it follows that the change in the ionic strength of the medium in the estuarine environment changes the conformation of the riverine DOM (c.f. Gregory 1989). Interestingly, this is similar change that is caused by heterotrophic degradation (Figure 1), indicating exudation of humic-like DOM as a result of bacterial activity (Kothawala et al. 2012; Shimotori et al. 2012). Both change in the salinity and heterotrophic degradation obviously cause a portion of non-fluorescent DOM to modify to fluorescent DOM. This phenomenon has potential implications when using humic-like optical properties as a proxy for tracing terrigenous organic matter along the estuarine gradient (Baker and Spencer 2004; Fellman et al. 2011), as these findings suggest that the humic-like signal of DOM is perhaps not as stable as previously assumed.

4.4 Climate change drivers of DOM loading (papers I-IV)

A seasonal variability in the quantity and quality of DOM loading was evident in all of the estuaries (I, III). However, in spite of the changing properties of the DOM pool, its bacterial degradation was not affected by temperature (II). In the predicted future climate, an increasing temperature, however, is likely to enhance the carbon flow to the microbial food web to some extent and may thus shift the balance between auto- and heterotrophs towards more heterotrophic system (von Scheibner et al. 2013). But even more significant effects of the climate change will be caused by the increasing precipitation in the boreal areas, as the annual-scale DOM flux from various land use types (agriculture, forest, peatland) is controlled mostly by hydrology (i.e. discharge, not temperature, Pastor et al. 2003; Jiang et al. 2013). Also, in the wetter and warmer future climate in boreal areas, river discharges are expected to increase and a longer ice-free period will supply freshwater to estuaries more evenly throughout the year (Schneider et al. 2013).

Increased precipitation leads to higher river discharges, and subsequently to decreased water residence time in the catchments and the limnic systems (Scheider et al. 2013). Decreasing water residence time causes also decrease in the degradation processes (i.e. photolysis and biodegradation), which in turn result as increased "browning" of the aquatic systems (Köhler et al. 2013). A consequence is that the bulk DOM is less altered once it reaches

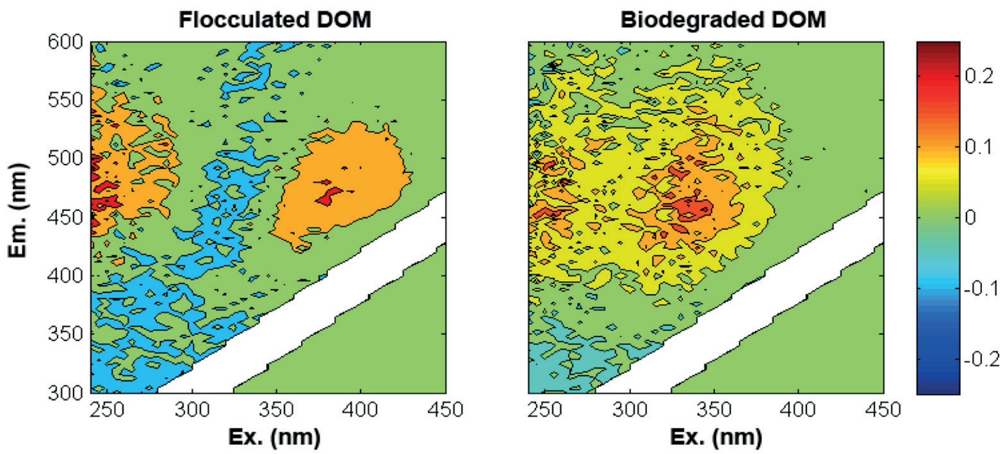

Figure 1. Net change in fluorescence excitation-emission matrices (in raman units) of riverine DOM after a) addition of salt to reach final salinity 4 (III), and b) 39-d degradation by estuarine bacteria in dark (IV). Turquoise-blue colors indicate net loss of fluorescence, and yellow-red colors indicate increase of fluorescence in that particular part of the EEM. Green color means no change.

the estuarine environment and is more similar to fresh, terrigenous DOM. In our study, decreased predegradation increased the bacterial growth efficiency (IV), which indicates that fresher DOM could be transferred to aquatic food web more efficiently than more extensively processed DOM. This has potentially effects on coastal food webs, as higher quality DOM (for heterotrophic utilization) is discharged from the rivers. Also, as the DOM entering the estuaries is likely to be less processed, and its susceptibility to flocculation will be increased thereby potentially increasing the allochthonous organic matter loads to coastal sediments.

The residence time and the resulting quality of the riverine DOM are dependent on the catchment characteristics and land-use practices. For instance, higher catchment water storage potential leads to lower organic matter loading, which also affects the sensitivity to climatic oscillations (Pastor et al. 2003; Mengistu et al. 2013). Furthermore, land-use practices that increase the water residence time in the catchments (such as riparian forests) also increase the extent of organic matter cycling before discharge to aquatic system (Lowrance et al. 1984; Nagasaka and Nakamura 1999). In order to reduce the impacts of climate change that are expected to increase the organic matter loading, likely the most effective strategy is to manage the catchment land-use to achieve increased water residence time and thus enhance the so-called reactive transport (Malik and Gleixner 2013).

4.5 Implications and future direction

A major issue in aquatic biogeochemistry is how to link DOM quality to biogeochemical processes (Jaffé et al. 2008; Köhler et al. 2012). Even though researchers generally acknowledge the importance of DOM quality, a coherent view linking DOM quality to the various transformation and removal processes is still incomplete. Findings from this thesis emphasize that DOM quality has a pivotal role in two essential and ubiquitous mechanisms that remove or transform DOM, biodegradation and flocculation. However, theoretical models may overlook DOM heterogeneity and assume constant rates of heterotrophic uptake or flocculation of organic matter. This discrepancy highlights the dangers of focusing on "quantity over quality" when considering the influence of organic matter loading to coastal seas and when using bulk properties to guide management. Conceptual understanding of DOM dynamics in catchment-coastal sea continuum is needed for ecosystem process management and restoration, as interventions to only in-stream or coastal processes are insufficient, emphasizing the need for catchment-scale interventions (Bernhardt and Palmer 2011; Juckers et al. 2013). Here are some important aspects that future studies could more explicitly consider in combination when interpreting results regarding the fate of DOM in estuaries:

- <u>Continuous measurements of riverine DOM load</u> by automated *in situ* optical methods would provide high-frequency data about the temporal variance of DOM quantity and quality. This data would allow research of sporadic events such as spring flood, which rapidly change the DOM concentrations and composition in rivers draining to the Baltic Sea.
- <u>Link DOM bioavailability to more specific chemical characteristics</u>. The shortcomings of optical measurements (such as exclusion of non-colored DOM) should be supplemented with other modern analysis techniques which provide detailed information about the composition and characteristics of the bioavailable fraction of DOM.
- <u>Trace pathways of riverine DOM in estuarine food webs</u> to assess the role of allochthonous matter in relation to autochthonous, phytoplankton-originated organic matter in coastal seas. Riverine inputs of DOM and the subsequent flocculating organic matter provides additional subsidies to heterotrophic food webs, which has consequences for organic matter cycling in the environment.

- Formulate DOM management strategies, which could be used for more accurate, targeted nutrient reductions. Current knowledge on causes, amounts and consequences of organic matter loading lags behind compared to that of inorganic nutrients. The plausible management actions are largely concurrent with inorganic nutrient reduction and include vegetation buffer zones between croplands/pastures and aquatic system, reduced dredging of peatlands and forests and controlled use of sloped land. If larger amount of organic matter was retained and degraded already within the catchment and the remaining fraction thus less reactive, the projected increase in heterotrophic secondary production and consequent food web changes could be avoided.

5 Conclusions

Riverine DOM entering the Baltic Sea is shaped by the catchment-scale processes, which affect both DOM quantity and quality. Proportion of forests and peatlands tend to increase the amount of DOC leaching from the catchments to the waterways, while lakes in the catchments reduce the organic matter loading. Forests and peatlands in the catchment can also be linked to humic-like properties of DOM, which are less distinct if proportion of lakes in the catchment is large. Agriculture in the catchment area results as relatively high DON loading, and also increasing the availability of inorganic nutrients in the system, thus affecting the DOM cycling. Seasonal variation of DOM quantity and quality in the study catchments indicate dilution of DOM concentrations by the spring freshet and pronounced terrestrial signal in the autumn.

Bioavailability of DOM could be linked to its qualitative properties, such as humic-like fluorescence, aromaticity and molecular weight. In summary, DOM pool consisting of large, humic-like constituents was less favorable than DOM pool with smaller, less humic-like compounds. The poorer quality of DOM resulted as lower bacterial growth efficiency and higher C:N uptake ratio, which indicates less efficient performance of the heterotrophic food web as a response to the inferior DOM quality. Resulting from the performance of heterotrophic bacteria, the DOM quality also has effects on carbon cycling in the aquatic systems, as poorer quality substrate transfers less carbon to microbial food web and more to CO_2 emissions.

Flocculation of riverine DOM in estuaries was found to be a significant removal and transformative process, occurring already at upper estuaries. This sensitivity of DOM flocculation to low salinities was quantified by a mechanistic model, which revealed the significant increase in flocculation affinity of DOM at very low salinities. The salt-induced flocculation process was confirmed to be highly selective, removing most efficiently DOM containing iron. Continuous flocculation of riverine DOM and consequent sedimentation of organic matter has potentially significant impacts on benthic food webs, providing a replete source of allochthonous organic matter.

Both biodegradation and flocculation remove riverine DOM entering the estuaries, but also shape the properties of the remaining DOM pool reaching the open sea. As the bulk DOM is simultaneously being processed by heterotrophic degradation and flocculation, DOM constituents are being selectively removed from the DOM pool. Also, both processes shape the remaining bulk DOM pool, with transformations of DOM constituents or introduction of additional constituents (such as extracellular enzymes). The resulting DOM pool in the lower estuaries is significantly different than the riverine DOM that entered the estuary, as the most bioavailable and the most easily flocculated compounds are removed from the DOM pool.

Yhteenveto

Jokiperäinen liuennut orgaaninen aines (*dissolved organic matter*, DOM) on tulosta valuma-alueen monimutkaisten prosessien yhteisvaikutuksista, yhdistäen maa- ja rannikkosysteemit kuljettamalla eloperäistä ainesta valuma-alueelta jokisuistoihin. Tässä työssä on yhdistetty kenttähavaintoja ja laboratoriokokeita jokiperäisen DOM:in määrän ja laadun vaihtelun arvioimiseen kolmessa Itämereen laskevan joen suistossa. Lisäksi työssä tutkittiin DOM:in koostumukseen vaikuttavia biogeokemiallisia muutos- ja poistoprosesseja. Valuma-alueen ominaisuuksia pystyttiin yhdistämään jokiperäisen DOM:in koostumukseen. DOM:in laatua arvioitiin tutkimuksessa useilla analyyseillä: C/N stoikiometrialla, värillisen eloperäisen aineen (*colored dissolved organic matter*, CDOM) absorptiolla ja fluoresenssilla, molekyylipainolla ja rautapitoisuudella. Jokisuistojen DOM altistettiin heterotrofiselle bakteerihajotukselle faktorityyppisissä koejärjestelyissä saliniteetin, epäorgaanisten ravinteiden ja esihajotuksen vaikutusten DOM:in biohajoavuuteen ja bakteeriyhteisön toiminnan tutkimiseksi. Lisäksi suolan aiheuttamaa DOM:in sakkautumista tutkittiin yhdistämällä kenttähavaintoja, laboratoriokokeita ja mallinnusta. Kolme tutkittavana ollutta valuma-aluetta erosivat merkittävästi maankäytöltään, ja nämä muutokset heijastuivat jokiperäisen DOM:in määrään ja laatuun. Vuodenaikaisvaihtelua havaittiin sekä DOM:in määrässä että laadussa, mutta vaihtelu ei vaikuttanut DOM:in biologiseen hajotukseen. Laboratoriokokeet vahvistivat metsä- ja suopinta-alan vaikuttavan lisäävästi valuma-alueiden hiilivirtoihin, mutta vähentävän biohajoavan liuenneen eloperäisen hiilen (*dissolved organic carbon*, DOC) suhteellista osuutta ja heikentävän bakteerikasvutehoa (*bacterial growth efficiency*, BGE). Maatalousmaan suuri suhteellinen osuus valuma-alueella voitiin yhdistää korkeaan liuenneen eloperäisen typen (*dissolved organic nitrogen*, DON) kuormaan ja biohajoavuuteen. Järvien suhteellisesti suuri määrä valuma-alueella taas alensi DON:in biohajoavuutta. Laboratoriokokeissa suolapitoisuuden ei havaittu vaikuttavan DOM:in biohajoavuuteen eikä BGE:hen. Myöskään epäorgaanisten ravinteiden lisäys ei kasvattanut biohajoavuutta, mutta nosti bakteerikasvutehoa keskimäärin 11 prosentista 40 prosenttiin. Esihajotus, eli DOM:in altistaminen vaihtelevalle jaksolle heterotrofista bakteerihajotusta ennen varsinaisia hajotuskokeita, laski kasvutehoa keskimäärin 65 prosentista 25 prosenttiin. Sakkautuminen aiheutti poikkeamia DOM:in konservatiivisesta sekoittumisesta tutkituissa jokisuistoissa, ja sakkautuvan DOM:in määrää ja laatua tutkittiin laboratoriokokeessa. Suurin havaittu poikkeama DOC-pitoisuudessa konservatiivisen sekoittumisen odotusarvosta oli -16% suolapitoisuuden ollessa välillä 1–2, joka kertoo merkittävästä sakkautumisesta suhteellisen kapealla suolapitoisuuden vaihteluvälillä. Molemmat prosessit, biohajotus ja sakkautuminen, poistivat jokiperäistä DOM:ia ennen sen kulkeutumista merelle, mutta myös muuttivat jäljelle jääneen DOM:in ominaisuuksia. Molemmat prosessit myös lisäsivät DOM:in humustyyppistä fluoresenssia ja ominaisabsorbanssia, mistä voidaan päätellä että merelle saakka päätyvä, vaikeasti hajotettava DOM on tulosta monista vuorovaikutteisista prosesseista matkalla maalta merelle. Kaiken kaikkiaan sekä biohajotus että sakkautuminen poistavat DOM:ia jokisuistoissa, mutta myös muuttavat jäljelle jäänyttä DOM:ia. Tämän tutkimuksen tulokset osoittavat että DOM:in laadulla on suurta merkitystä näiden keskeisten ja yleisten mekanismien toimintaan.

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